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Low Voltage Operation of the Ferroelectric Pb(Zr, Ti)O_3 Capacitors Derived by Sol-Gel Method

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1. Introdction

Ferroelectric memory (FeRAM: ferroelectric random access memory) has been expected as a non-volatile RAM, and FeRAMs has been produced in mass production level already. Embedded FeRAMs have been intensively studied because the FeRAM has high potential for low-power, high-speed operation, and high switching endurance compared to conventional non-volatile memories. To realize the embedded FeRAMs, reducing the temperature during fabrication of the ferroelectric capacitors is essential not to affect the parameters of MOS transistors, especially in a fine design rules. Reducing the operation voltage is also essential for low power consumption and high speed operation.

The Pb(Zr,Ti)O_3 ferroelectric derived by sol-gel method were widly used as a ferroelectric capacitor of the FeRAMs. The sol-gel PZT has advantages of controllability of composition, especially lead composition, and uniformity of film thickness and reproductivity. Therefore high yield can be easily obtained in the FeRAM production. But the sol-gel PZT has some disadvantages of relative high crystallization temperature (above 700°C) and high operating voltage.

In this study, these disadvantages were overcome by using low pressure annealing and two steps annealing techniques.

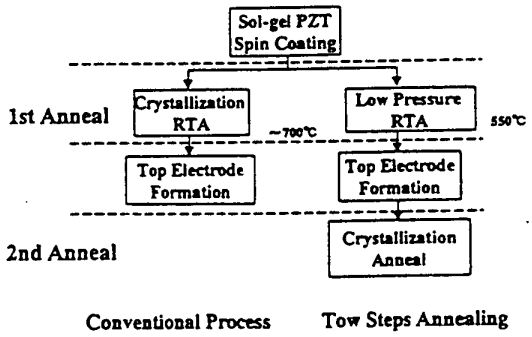

Figure 1: Flow diagram for film crystallization

2. Experimental Procedure

PZT ferroelectric thin films were prepared by the conventional sol-gel method.[1] A solvent of the sol-gel solution is 2-metoxyethanol and the Zr/Ti ratio of the sol-gel precursor is 52/48. Si(p-type) wafers were used as the substrates. Pt(175 nm)/IrO_2(65 nm) was deposited as the bottom electrodes by magnetron sputtering. After spin coating of PZT precursor, the films were baked at 200°C to evaporate the solvent and preannealed at 400°C in dry air to eliminate organic components. These processes were repeated several times until the film thickness became 150 or 300 nm. The deposited films were crystallized by using low pressure rapid thermal annealing (RTA) and two steps annealing technique. Ir based top

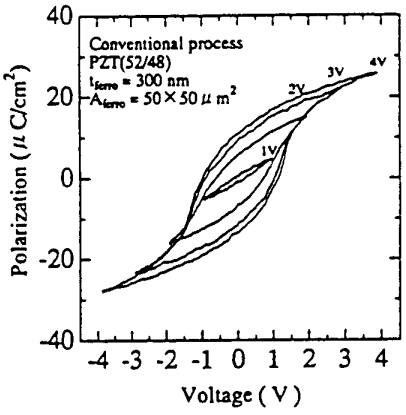

Figure 2: D–E hysteresis loops of conventional crystallization process

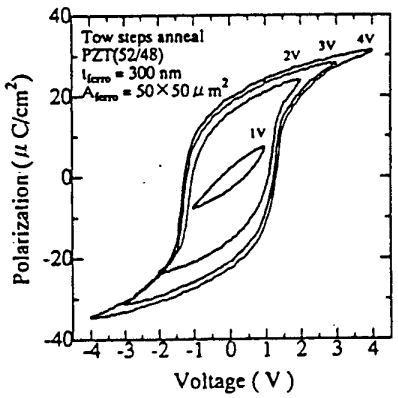

Figure 3: D–E hysteresis loops of two steps crystallization process

electrode was deposited by sputtering and patterned by dry etching. The area of the top electrode is $50 \times 50 \mu m^2$.

Figure 1 shows a flow diagram for ferroelectric film crystallization process. In the conventional crystallization process, the spin coated films were crystallized by RTA (first anneal). Then the top electrodes were deposited. In the case of two steps annealing process, the films were annealed by RTA with low pressure in oxygen, typically the oxygen pressure is 15 Torr (first anneal). Then the top electrodes were formed. Finally the crystallization anneal was carried out by RTA under normal pressure (760 Torr) oxygen at 675°C for 1 min.

In the case that first low pressure annealing is not carried out, gas come out from the films during crystallization, and the top electrodes peel off and the crystallized films contain many bubbles. The *D–E* hysteresis loops and switching charges were measured by a conventional Sawer–Tower circuit.

3. Results and Discussions

D–E hysteresis loops of conventional crystallization process is shown in Fig. 2. The first anneal was carried out as the crystallization anneal by normal pressure RTA. Figure 3 shows *D–E* hysteresis loops of two steps crystallization process. The coated films were annealed by the low pressure RTA, and then the top electrode was formed. Finally, crystallization RTA at 675°C was carried out. In the case of two steps annealing, the shape of the hysteresis loops became more rectangular one, and a saturation characteristic of polarization was also improved. Figure 4 shows the *D–E* hysteresis loops of the 150 nm thick PZT capacitors. Saturated hysteresis loops were obtained and the remanent polarizations were almost saturated over 2 V applied voltage. The saturation characteristic of the 150 nm thick PZT capacitors is shown in Fig. 6. The saturation voltage is 1.8 V.

The fatigue characteristic of the switching charge is shown in Fig. 6. The ±3 V (200 kV/cm) fatigue pulses were applied up to 10^{10} cycles. The switching charges were measured by ±3 V pulse trains those duration is 1 μs and interval is 1 s. From Fig. 6, the PZT capacitor show no fatigue up to 10^{10} cycles.

4. Conclusion

Sol-gel derived PZT capacitors were prepared by using low pressure annealing and two steps annealing technique. By using these technique, the saturation characteristics of the PZT films were improved. The saturation voltage is 1.8 V with 150 nm PZT thin films, The low voltage operation and no imprint PZT capacitors were obtained by using two steps annealing techniques with low pressure.

References

1) T. Nakamura, Y. Nakao, A. Kamisawa and H. Takasu: Jpn. J. Apply. Phys. **33** (1994) 5207.

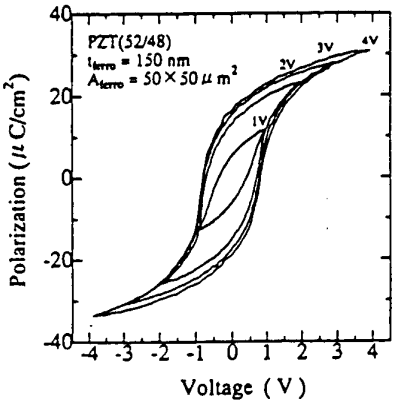

Figure 4: *D–E* hysteresis loops of 150 nm thick PZT capacitors

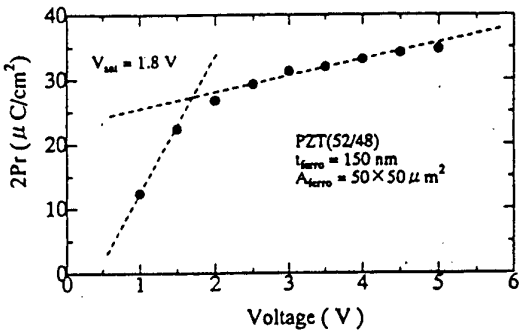

Figure 5: Saturation characteristics of polarization of 150 nm PZT capacitors

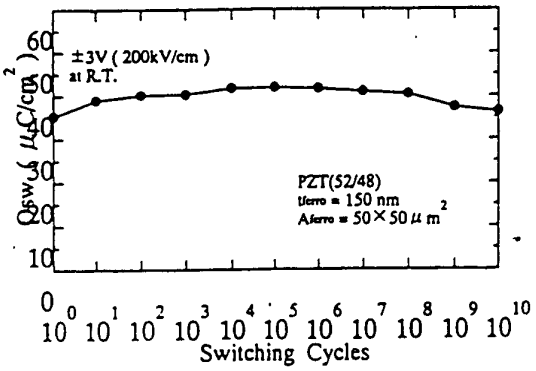

Figure 6: Fatigue characteristics of 150 nm PZT capacitors